

- (19) Japan Patent Office (JP)  
(11) Patent Application Publication  
(12) Laid-open Patent Application Publication (A) S 62-297463

(51) Int. Cl. <sup>4</sup>	Identification Code	File No.
C 23 C 14/34		8520-4K
C 22 F 9/20		G-6554-4K
C 22 C 1/04		E-7511-4K
27/02	103	6411-4K
C 23 C 13/13		8520-4K

(43) Publication Date: 12/24/1987  
Examination not yet requested  
Number of Inventions: 3 (Total of 11 pages)

(54) Name of Invention: High-purity Metallic Tantalum Target and Manufacturing Method Thereof

(21) Patent Application: S 61-133802

(22) Application Date: 6/11/1986

(72) Inventor:

Iwao Kyono  
Nippon Mining Co.  
Central Research Laboratories  
3-17-35 Niizominami, Toda City

(72) Inventor:

Hiroshi Hosaka  
Nippon Mining Co.  
Central Research Laboratories  
3-17-35 Niizominami, Toda City

(72) Inventor:

Yaegashi Seiji  
Nippon Mining Co.  
Central Research Laboratories  
3-17-35 Niizominami Toda City

(71) Applicant:

Nippon Mining Co.  
1-12-32 Akasaka, Minato-ku, Tokyo

(74) Representative: Motoyuki Kurauchi, Patent Attorney, and one other

Specification

1. Name of Invention

High-purity Metallic Tantalum Target and Manufacturing Method Thereof

2. Patent Claims

- 1) A high-purity metal tantalum target, wherein the alkali metal concentration is no more than 50ppb, the radioactive element concentration is no more than 5 ppb, the transition metal concentration is no more than 3ppm, and the high-melting-point metal concentration is no more than 3 ppm.

EV085429915

- 2) A method for manufacturing a high-purity metal tantalum target, wherein the alkali metal concentration is no more than 50ppb, the radioactive element concentration is no more than 5 ppb, the transition metal concentration is no more than 3ppm, and the high-melting-point metal concentration is no more than 3 ppm, said method comprising:
  - (i) Production of an aqueous solution containing tantalum by dissolving metallic tantalum or tantalum pentoxide in hydrofluoric acid or a mixed acid solution containing hydrofluoric acid;
  - (ii) Separation of tantalum potassium fluoride crystals by adding an aqueous solution containing potassium ions to said tantalum-containing aqueous solution;
  - (iii) Sodium reduction on the recovered tantalum potassium fluoride crystals to produce a product including metallic tantalum powder, potassium fluoride, and sodium fluoride;
  - (iv) Rinsing of said product to recover the metallic tantalum;
  - (v) Production of a metallic tantalum ingot by pressure forming and sintering, and then fusing, the recovered metallic tantalum powder; and
  - (vi) Processing the metallic tantalum ingot into a target.
- 3) A method according to Claim 2, characterized by the pressure forming and sintering, and then melting being performed through cold isobaric pressurization and hot isobaric pressurization and electron beam melting.
- 4) A method for manufacturing a high-purity metal tantalum target, wherein the alkali metal concentration is no more than 50ppb, the radioactive element concentration is no more than 5 ppb, the transition metal concentration is no more than 3ppm, and the high-melting-point metal concentration is no more than 3 ppm, said method comprising:
  - (i) Production of an aqueous solution containing tantalum by dissolving metallic tantalum or tantalum pentoxide in hydrofluoric acid or a mixed acid solution containing hydrofluoric acid;
  - (ii) Separation of tantalum potassium fluoride crystals by adding an aqueous solution containing potassium ions to said tantalum-containing aqueous solution;
  - (iii) Production of a tantalum hydrate through adding the separated tantalum gallium fluoride crystals into an ammonia solution, producing an aqueous solution containing tantalum by dissolving the separated tantalum hydrate in hydrofluoric acid, separating tantalum potassium fluoride crystals by adding an aqueous solution containing potassium to said aqueous tantalum solution, and repeating the process as necessary;
  - (iv) Sodium reduction on the recovered tantalum potassium fluoride crystals to produce a product including metallic tantalum powder, potassium fluoride, and sodium fluoride;
  - (v) Rinsing of said product to recover the metallic tantalum;
  - (vi) Production of a metallic tantalum ingot by pressure forming and sintering, and then fusing, the recovered metallic tantalum powder; and
  - (vii) Processing the metallic tantalum ingot into a target.
- 5) A method according to Claim 4, characterized by the pressure forming and sintering, and then melting being performed through cold isobaric pressurization and hot isobaric pressurization and electron beam melting.

### 3. Detailed Explanation of the Invention

#### Area of Application in Industry

The present invention relates to high-purity metallic tantalum (Ta) targets and manufacturing methods thereof, and in particular, relates to high-purity metallic tantalum targets used in sputtering in order to fabricate tantalum oxide layers ( $Ta_2O_5$  layers) for use in semiconductor devices, along with the manufacturing method thereof. In the  $Ta_2O_5$  layer that is fabricated using the tantalum target of the present invention, the impurities that can have a damaging

effect on the semiconductor device are reduced to extremely small quantities, which is extremely desirable in insulating layers in semiconductor devices. In addition, the tantalum target according to the present invention is desirable in the fabrication of electrodes for ICs.

### Background of the Invention

Conventionally, the silicon oxide layers ( $\text{SiO}_2$  layers) have been used as the interlayer insulating layers between electrode interconnects in semiconductor devices; however, the performance of silicon oxide layers is inadequate for the thinner insulating layers that go along with the higher levels of integration in ICs, so there have been many attempts to use tantalum oxide layers ( $\text{Ta}_2\text{O}_5$  layers) because of the higher dielectric constant. There is also an intense focus at present on this high-dielectric constant  $\text{Ta}_2\text{O}_5$  as a dielectric for capacitors for large-scale MOS DRAM (Dynamic Random Access Memory). This type of  $\text{Ta}_2\text{O}_5$  layer typically is fabricated through sputtering a tantalum target in an argon-oxygen mixed-gas ambient; however, the sputtered  $\text{Ta}_2\text{O}_5$  thin films tend to pass leakage currents because they contain many trap nucleation sites. The cause of the leakage current is thought to be mainly due to residual impurities. Consequently, in order to reduce the leakage current, it is necessary to reduce the residual impurities.

Furthermore, in order to improve the reliability of the performance of the semiconductor device elements, it is necessary to reduce impurities such as:

- (1) Alkali metals such as Na, K, and Li,
- (2) Radioactive elements such as U and Th,
- (3) Transition metals such as Fe, Cr, Ni, and Mn.

The alkali metals such as Na are highly mobile in the gate insulation layers, damaging the interfacial properties, while radioactive elements such as U have a fatal effect on the reliability properties of the elements due to the alpha rays radiated from the elements. Fe and other transition metals also compromise the reliability of the operation. For these reasons, in materials used to structural VLSI circuits, it is imperative that alkali metals, radioactive elements, transition metals, and other impurities be reduced.

In addition to the aforementioned  $\text{Ta}_2\text{O}_5$  insulating layer, there is also research underway regarding the use of metallic tantalum layers for electrode layers such as LSI gate electrodes, source electrodes, and drain electrodes. Conventionally, conventional polycrystalline silicon has been used as this type of electrode, but, because of an awareness of problems with signal propagation delays and problems with the fabrication of MOS elements using a self-alignment method, there is a great deal of testing into the use of high-melting-point metals with lower resistance than polycrystalline silicon, and active testing of silicides thereof. One powerful candidate metal, along with tungsten and molybdenum, etc., is tantalum. These tantalum electrodes, of course, also require reduced concentrations of the impurities such as described above.

Whether metallic tantalum is used or whether tantalum oxides are used, the layers are typically formed using sputtering methods and vapor deposition methods. In sputtering methods, a metal target plate is bombarded with argon ions to cause it to discharge the metal, where the metal that is discharged accumulates on a substrate opposite the target. On the other hand, in electron beam vapor deposition methods, a vapor source is melted by an electron beam to cause vapor deposition. As a result, the purity of the layer produced is determined by the purity of the target plate or of the vapor source. Consequently, the creation of a high-purity metal tantalum layer or a  $\text{Ta}_2\text{O}_5$  layer requires high purity levels in the sputtering target plate or the electron beam vapor deposition source used as the raw material. Note that in this description, plate-shaped tantalum materials or other shapes of tantalum materials used as sputter sources or vapor deposition sources will be termed, inclusively, "tantalum targets."

### Prior Art and Problems Therein

The tantalum targets available on the market today are formed, sintered, and then fused from off-the-shelf metallic tantalum powder with a purity of 99.9%, after which mechanical processing is performed to manufacture the tantalum target. The impurity levels are, typically, no more than 100ppb for alkali metals such as Na and K, no more than 5ppb for radioactive elements such as U, and no more than 1ppm for transition metals such as Fe, Ni, Cr, and Mn, and there are no particular problems with these impurity levels.

However, recently, the existence of high-melting-point metal impurities such as Nb, Mo, W, Sr, and Hf have attracted attention as well. The inclusion of Nb in tantalum targets available on the market is in the order of tens of ppm, and the concentrations of Mo, W, Zr, etc., is between 1 and 10ppm. The amount of these high melting-point metal impurities is two orders of magnitude higher than in the other materials such as silicon and molybdenum comprising the IC. As a result, if the amounts of these impurities included in the material are not reduced by two orders of magnitude, then the material would not be appropriate for use in electronic device element structures, which require increasingly high levels of reliability.

### The Object of the Invention

In view of the above, the object of this invention is to establish a method for manufacturing a high-purity metal tantalum target with extremely low concentrations of high melting-point metals included therein, in addition to extremely low levels of alkali metals, radioactive elements, and transition metals.

### Summary of the Invention

The result of extensive investigations directed at this object was the conclusion that it is impossible, when eliminating the high melting-point metal impurities, to use a wet method of crystal formation for eliminating the high melting-point metal impurities from the tantalum (and tantalum compounds) sold on the market today. While it is possible to eliminate alkali metals and transition metals through the use of an electron beam melting process, the high melting-point metals cannot be eliminated through electron beam melting. One may consider several methods as wet refining methods. For example, one may consider first a (1) ion replacement method and (2) a solvent distillation method. However, in the (1) ion replacement method, even though it is possible to separate the Nb, Mo, W, Zr, and Ti, because Ta is the element to be deposited, such a process is thought to be costly and thought to have low productivity. The solvent distillation process of (2) is a process that is performed in industry with MIBK as the distilling material, but because the ignition temperature of the solvent is low, there are safety problems with this method.

Given the above, the present inventors determined that the use of a discrete crystal process that uses a differences in solubility to cause the tantalum compounds to crystallize first in a wet refining process, followed by a reduction of the tantalum compound produced is the optimal process for producing tantalum powder, and so the present inventors performed more research on these processes. The result was that an excellent refining effect was obtained through reducing tantalum potassium fluoride crystals ( $K_2TaF_7$ ) followed by sodium reduction.

The high-purity tantalum powder obtained through this type of wet refining can be made into a final tantalum target through the use of a forming/sintering/fusing manufacturing process followed by a machining process. The highest purity level is obtained through the use of an electron beam method as the method for fusing.

Ultimately, an ultra high-purity tantalum target is produced with an alkali metal concentration of no more than 50ppb, a radio active element concentration of no more than 5ppb, a

transition metal concentration of no more than 3ppm, and a high melting-point metal concentration of no more than 3ppm.

In this way, the present invention is a high-purity metal tantalum target wherein the alkali metal concentration is no more than 50ppb, the radioactive element concentration is no more than 5ppb, the transition metal concentration ratio is no more than 3ppm, and the high melting-point metal concentration is no more than 3ppm, and is a method for manufacturing the same, providing a method for manufacturing a high-purity metal tantalum target, where said method includes:

- (i) Production of an aqueous solution containing tantalum by dissolving metallic tantalum or tantalum pentoxide in hydrofluoric acid or a mixed acid solution containing hydrofluoric acid;
- (ii) Separation of tantalum potassium fluoride crystals by adding an aqueous solution containing potassium ions to said tantalum-containing aqueous solution;
- (iii) Sodium reduction on the recovered tantalum potassium fluoride crystals to produce a product including metallic tantalum powder, potassium fluoride, and sodium fluoride;
- (iv) Rinsing of said product to recover the metallic tantalum;
- (v) Production of a metallic tantalum ingot by pressure forming and sintering, and then fusing, the recovered metallic tantalum powder; and
- (vi) Processing the metallic tantalum ingot into a target.

In order to increase the refining effect, a step can be added between the steps (ii) and (iii), above, wherein there is production of a tantalum hydrate through adding the separated tantalum gallium fluoride crystals into an ammonia solution, producing an aqueous solution containing tantalum by dissolving the separated tantalum hydrate in hydrofluoric acid, separating tantalum potassium fluoride crystals by adding an aqueous solution containing potassium to said aqueous tantalum solution, and repeating the process as necessary;

In the present invention, "alkali metal" indicates the metals belonging to the IA group in the periodic table, represented by Na, K, and Li. "Radioactive elements" indicate elements that can radiate, such as U, Th, and so forth. "Transition metals" refers to those [ILLEGIBLE] transition elements that are metal elements with relatively low melting points, including Fe, Cr, Ni, and Mn. The "high melting-point metals" indicate the [ILLEGIBLE] transition metals that have relatively high-melting-points, including Nb, Mo, W, Zr, and Hf.

#### Detailed Explanation of the Invention

Figures 1 to 3 show a fundamental flow chart of the present invention, along with a preferable example embodiment thereof. These are referenced in the explanation below.

As described above, the tantalum targets on the market include high melting-point impurities even in the order of several dozen ppm. As the method for refining these high melting-point metal impurities out, metallic tantalum or a tantalum compound such as pentoxy tantalum, as sold on the market, is used as the starting material, and the material must be put into a wet refining process that begins with dissolving the material to form an aqueous solution. First, for the purposes of explanation (while referencing Figure 1), the impurities to be removed in the wet refining process are, primarily, high melting-point metals and radioactive elements, and here tantalum potassium fluorine crystals ( $K_2TaF_{[ILLEGIBLE]}$ ) are obtained. Next, said crystals are subjected to sodium reduction to produce a high-purity tantalum powder. After drying, the high-purity tantalum powder is formed and sintered, preferably, using cold isobaric pressure (CIP) or hot isobaric pressure (HIP), after which it is fused, preferable through the use of electron beam (EB) melting. Here the elements with vapor pressures higher than that of tantalum (in other words, alkali metals, radioactive elements, and transition metals) are removed. The tantalum ingot thus produced is machined and finished into a tantalum target.

It can be said that the characteristic features of the present invention are, fundamentally, that the invention combines a wet refining process and a dry process, where radioactive elements and high melting-point metals are removed in the former, and alkali metals, radioactive elements, and transition metals are also removed in the later.

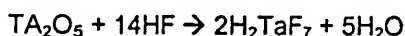
These processes will be explained separately. (See Figures 2 and 3):

#### (I) Tantalum Source Material

For the raw materials for the tantalum, materials that are as pure as possible and that can be dissolved easily in acid or alkali are preferable. Typically off-the-shelf metallic tantalum powder or pentoxide tantalum ( $\text{Ta}_2\text{O}_5$ ) is used. Conversely, tantalum compounds such as tantalum potassium fluoride can also be used.

#### (II) Dissolution

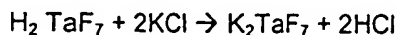
Although a method of dissolving in alkali or methods using a variety of inorganic acids can be listed as methods for dissolving, a preferable method is to use a hydrofluoric acid that can dissolve [the material] at a relatively low temperature of no more than  $100^\circ\text{C}$  and that can produce  $\text{K}_2\text{TaF}_7$  crystals. Fundamentally for metal tantalum powder, mixed acids of, for example, hydrofluoric acid and nitric acid is used, where  $\text{Ta}_2\text{O}_5$  is dissolved in hydrofluoric acid. The following reaction occurs for  $\text{Ta}_2\text{O}_5$ :



The amount of hydrofluoric acid used should be at least the theoretical amount, and more preferably, 13 to 15 times the theoretical amount should be used. Additionally, the dissolution temperature should be at least  $60^\circ\text{C}$ , or more preferably, at least  $80^\circ\text{C}$ . When the amount of the hydrofluoric acid used is less than the amount described above, or if the dissolution temperature is less than the temperature described above, the  $\text{Ta}_2\text{O}_5$  will be difficult to dissolve, affecting the efficiency.

#### (III) Obtaining the Crystals

The tantalum-containing aqueous solution is filtered to separate out the solid impurities. The solution for causing a formation of the crystals is gradually added to the solution containing potassium ions such as KCL.  $\text{K}_2\text{TaF}_7$  is produced through the following reaction:



The amount of potassium chloride used when crystallizing the tantalum potassium fluoride is at least one times the theoretical amount, and preferably between 11 and 14 times the theoretical amount. Also the temperature should be at least  $60^\circ\text{C}$ , and, preferably between  $80^\circ\text{C}$  and  $95^\circ\text{C}$ . If the amount of potassium chloride used is less than what is described above, the crystallization rate of the tantalum potassium fluoride will be diminished. On the other hand, if the temperature is lower than that which is described above, the tantalum potassium fluoride crystals will be too small, making them difficult to filter and rinse.

After filtering the tantalum potassium fluoride crystals, the crystals are rinsed thoroughly in a potassium fluoride solvent until the pH reaches about 5 to 6, after which the material is dried.

If further refining is desired, aqueous ammonia is added to the tantalum potassium fluoride crystals to generate tantalum hydride, where tantalum hydride is precipitated,

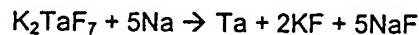
rinsed, and dried to produce tantalum pentoxide. A tantalum-containing aqueous solution obtained by again dissolving said tantalum pentoxide in hydrofluoric acid is added to a solution containing potassium ions to produce tantalum potassium fluoride crystals. After rinsing and filtering, the material is rinsed in a potassium fluoride solvent, and is then dried. In some cases, the step described above is repeated.

In the wet processing described above, clean, chemical resistant tools, such as the reaction vessel and the filter, should be used, and the water and chemicals used should also be of high purity levels.

#### (IV) Reduction

The high purity tantalum potassium fluoride crystals obtained in the wet processes described above are then reduced. The tantalum potassium fluoride can be reduced easily using highly-reactive metals such as Ti, Al, Mg, or Na; however, for industrial purposes, it is Na that is usually used as the reducing agent. The same is true in this invention. Na does not form a compound with Ta, and so a Na reduction method is used because the Na does not contaminate the metal Ta product and because it is relatively easy to eliminate the NaF byproduct.

There are no particular constraints pertaining to the Na reduction, and conventional methods may be used. The following equation shows the reaction between the tantalum potassium fluoride and the Na, a reaction that is exothermic:



In the reaction above, an alkali halide such as NaCl is usually added as a diluting agent in order to reduce the temperature and stabilize the reaction.

After the reaction, the metal tantalum powder, the sodium fluoride, and the potassium fluoride products will be precipitants at the bottom of the reaction chamber.

The products that are recovered are first rinsed in ethanol, rinsing away any unreacted metallic sodium as sodium ethylate, after which warm water is used to eliminate the sodium fluoride and the potassium fluoride. After obtaining the metal tantalum powder, an appropriate rinsing process, such as a pressurized [sic – hot?] water rinse, a hydrofluoric acid rinse, an ammonia rinse, or an acetone rinse is performed, after which the material is dried.

Just as described above, the reactor vessel, the chemicals, and the environment must be clean.

#### (V) Pressure Forming, Sintering, and Fusing

The high-purity metal tantalum powder obtained by reducing the tantalum potassium fluoride is sent to an appropriate forming process so as to produce a tantalum ingot. The alkali metals, radioactive elements, and transition elements must be eliminated during fusing. Although refining technologies such as vacuum melting can be used to eliminate the impurities, the use of an electron beam melting process, with its excellent effectiveness in eliminating impurities, is preferred.

The product that is supplied to the electron beam melt must be free of the risk of internal air bubbles or contamination, and a pressurized die with a high apparent density should be used.

For example, the tantalum powder is loaded into a cylinder made from an appropriate material, and is subjected to cold isobaric compression using a compressive force between 1000 and 1600 kg/cm<sup>2</sup>. The molded material thus obtained is put into a mild steel container, is heated to a high temperature, and while outgassing under a vacuum, the mild steel container is sealed. The sealed mild steel container is placed in an isobaric pressurized device during heating, and is sintered at between 1000 and 1500°C under a pressure of between 900 and 1500 kg/cm<sup>2</sup>. After cooling, when the sintered tantalum unit is removed from the mild steel container, the unit makes a suitable electrode for use in electron beam melting. Next the sintered tantalum electrode is melted and fused using an electron beam to produce a tantalum ingot. The electron beam fusing can be repeated two or three times as necessary.

#### (VI) Machining

The tantalum ingot obtained is finally machined into a tantalum target of an appropriate shape. A conventional method is used in the shaping process, while using caution to prevent contamination during cutting and surface finishing.

The high purity metal tantalum target produced in this way is a high quality unit with an alkali metal concentration of no more than 50ppb, a radioactive element concentration of no more than 5ppb, a transition metal concentration of no more than 3ppm, and a high melting-point metal concentration of no more than 3ppm.

A Ta<sub>2</sub>O<sub>5</sub> layer is fabricated using sputtering in a mixed argon-oxygen gas environment, for example, using this tantalum target. The Ta<sub>2</sub>O<sub>5</sub> layer obtained does not contain damaging impurities, and thus it is possible to ensure excellent performance and operating reliability in semiconductor devices using the Ta<sub>2</sub>O<sub>5</sub> layers. Incidentally, the result of using the tantalum target of the present invention to fabricate a MOS capacitor with a Al/Ta<sub>2</sub>O<sub>5</sub>/P-Si structure using reactive sputtering in an Ar-O<sub>2</sub> mixed gas was a device wherein the leakage current was extremely small when compared to conventional devices.

#### Effects of the Invention

The present invention contributes to the progress of the electronics industry by making it possible to produce high-quality constituent parts, such as insulating layers and electrodes, in semiconductor devices that have ever-increasing levels of integration.

#### Example of Embodiment

11kg of off-the-shelf tantalum pentoxide powder was obtained, and after mixing with 18kg of high purity 50% hydrofluoric acid in a Teflon reactor vessel for 10 hours at a temperature of 80°C, the material was filtered using a 0.2μm Teflon Millipore filter to separate out the solid impurities to produce an aqueous solution containing tantalum.

Next 3kg of high-grade potassium chloride was dissolved in 18 liters of ultra pure water, and added gradually to 6 liters of the tantalum-containing aqueous solution after heating to 80°C to induce tantalum potassium fluoride crystals. Afterwards, a Teflon filter was used to separate the crystals, and the tantalum potassium fluoride crystals were rinsed with an aqueous solution containing 100g/l concentration of potassium fluoride.

After the tantalum potassium crystals were dried, they were heated and reduced using metallic sodium in an iron reaction chamber to produce metallic tantalum powder, potassium fluoride, and sodium fluoride. In other words, 5.50kg of tantalum potassium fluoride and 2.0kg of metallic sodium were used in a reduction process in an argon gas ambient heated to 800°C and then held at 800°C for three hours. Afterwards, the excess Na was removed using



the argon, and after a hot water rinse was used to remove the potassium fluoride and the sodium fluoride, an aqua regia rinse or a hydrofluoric acid rinse was performed to remove the impurities, after which the materials were dried to produce the metallic tantalum powder.

The metallic tantalum powder was formed using cold isobaric pressure at 1500 kg/cm<sup>2</sup> and then sintered using hot isobaric pressure 1000kg/cm<sup>2</sup> at 1400°C for one hour, after which the results were melted and fused, using an electron beam, to produce a high purity metallic tantalum target after machining. The resulting concentrations of impurities in the high-purity metallic tantalum target were as shown in Table 1.

Table 1

	Na/Ta	K/Ta	U/Ta	Fe/Ta	Nb/Ta	Mo/Ta	W/Ta	Zr/Ta
Tantalum pentoxide raw material	ppm --	ppm --	ppm <0.002	ppm <2.4	ppm 10	ppm 0.24	ppm 2.9	ppm <0.6
Tantalum potassium fluoride crystals	--	-	<0.003	<3	<1	<0.4	<0.6	<0.4
Metal tantalum powder	60	52	0.001	110	<0.2	<0.2	<0.3	<0.2
The metal tantalum target of the present invention	<0.02	<0.02	<0.001	0.1	<0.2	<0.2	<0.3	<0.2
A metal tantalum target available on the market	<0.05	<0.05	<0.001	0.1	50	2	10	1

As is clear from Table 1, the high-purity metallic tantalum target obtained in the present invention has a purity level of at least 99.999%, and when compared to the metallic tantalum targets available on the market, a high-purity metallic tantalum was obtained wherein, in particular, the high melting-point metals such as Nb, Mo, W, and Zr, each had concentrations of no more than 1ppm.

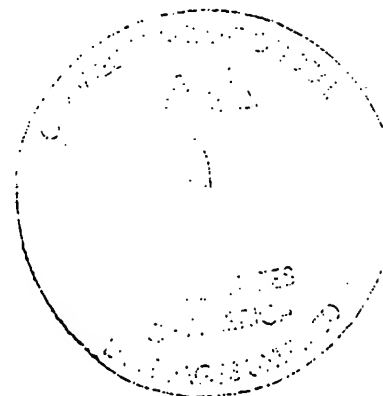
#### 4. Simple Explanation of Drawings

Figure 1 shows a basic flow chart of the tantalum target manufacturing method according to the present invention.

Figure 2 shows a flow chart for an example of embodiment of the process from the raw material Ta<sub>2</sub>O<sub>5</sub> powder to the K<sub>2</sub>TaF<sub>7</sub> crystal manufacturing.

Figure 3 shows a flow chart of an example of embodiment from the K<sub>2</sub>TaF<sub>7</sub> crystal through to the manufacturing of the Ta powder.

Name of Representative: Motoyasu Kuranaka  
Representative: Hiroshi Kazema



**Insert Fig. 1 on Page 324**

1. Ta source material (chemical compound)
2. HF mixture
3. Dissolution
4. Ta solution
5. K-ion solution
6. Crystallization
7. Removal of radioactive elements and high-melting-point metals
8. High-purity Ta chemical compound ( $K_2TaF_7$ )
9. Na reduction
10. High-purity Ta powder
11. Formation/sintering
12. Melting/Fusing
13. Removal of alkali metals and transition metals
14. Ta ingot
15. Machining
16. High-purity Ta target

**Insert Fig. 2 on Page 325**

1. HF dissolution
2. Filtering
3. HF solution
4. KCl solution
5.  $K_2TaF_7$  crystallization
6. KF solution
7. Filtering/rinsing of cake until Ph is approximately 5 to 6
8.  $K_2TaF_7$  crystals (wet)
9. Drying
10.  $K_2TaF_7$  crystals (dry)
11. Material to be reduced

**Insert Fig. 3 on Page 325**

12.  $K_2TaF_7$  crystals (dry)
13. Na reduction
14. Product
15. Ethanol
16. Na removal
17. Water or hot water
18. Water rinse
19. Removal of NaF, KF, NaCl until the Ph is about 8
20. Ta powder
21. Aqua regia
22. Aqua regia rinse
23. HF solution (about 1.5%)
24. HF rinse
25.  $NH_4OH$  solution (about 4%)
26. Ammonia rinse
27. ELS acetone
28. Acetone rinse
29. Drying
30. Ta powder

Amendment  
7/13/1987

To: Patent Office Director: Kunio Ogawa  
Name of Case: 1986 Patent Application 133802  
Name of Invention: High Purity Metallic Tantalum Target and Manufacturing Method Thereof.  
Amended By:

Relation to the Case:	Patent Applicant
Name:	Nippon Mining Co.
Representative:	
Name:	Motoyasu Kurachi, Patent Attorney (6781) [JUSTIFY??]
Address:	Yushi Kogyo Kaikan, 3-13-11 Nihonbashi, Chuo-ku, Tokyo
Telephone:	273-6436
Representative:	
Name:	Hiroshi Kazema, Patent Attorney (8577)
Address:	Same as above

Parts Subjected to Amendment:

Details description of the patent, drawings.

Details of Amendments: As attached.

The patent application 61-133802 specification shall be amended as follows:

1. Page 7, line 6: Correct "conventionally, this type of electrode" to say "as this type of electrode".
2. Page 8, line 5: Correct " $Ta_2O_2$ " to read " $Ta_2O_5$ ".
3. Page 10, line 6: Correct "Ti" to be "HF".
4. Page 11, line 8: Correct "tantalum target" to be "target made of tantalum."
5. Page 16, line 5: Replace "filter" with "filter" [SPELLED DIFFERENTLY IN JAPANESE]
6. Page 15, line 6: Correct "solution for crystallization" to be "crystallizing solution".
7. Page 16, line 19: Correct "filter" to read "filter" [SPELLED DIFFERENTLY IN JAPANESE]
8. Page 18, line 19: Correct "pressurized water rinse" to read "aqua regia rinse".
9. Page 18, line 20: Correct "ammonia rinse acetate rinse" to read "ammonia rinse, acetate rinse".
10. Page 9, line 2: Insert the following description between the end of the sentence and the beginning of the next sentence:

"This is because the inventors came to the realization that the high leakage current in the tantalum oxide was caused by electrical conductivity of the oxides of high-melting point metals and, in particular molybdenum and tungsten.."

11. Page 24, Table 1: Modify as shown below.
12. Replace Figure 3 with the attachment.

Table 1 (Units: ppm by weight)

	Na/Ta	K/Ta	U/Ta	Fe/Ta	Ni/Ta	Cr/Ta	Nb/Ta	Mo/Ta	W/Ta	Zr/Ta	Si/Ta
Tantalum pentoxide raw material	—	—	<0.002	<2.4	0.05	0.1	10	0.24	2.9	<0.6	—
Tantalum potassium fluoride crystals	—	—	<0.003	<3	—	—	<1	<0.4	<0.6	<0.4	—
Metal tantalum powder	60	52	0.001	110	0.7	0.8	<0.2	<0.2	<0.3	<0.2	—
The metal tantalum target of the present invention	<0.02	<0.02	<0.001	<0.02	<0.02	<0.02	<0.2	<0.2	<0.3	<0.2	0.1
A metal tantalum target available on the market	<0.05	<0.05	<0.001	0.1	—	—	50	2	10	1	—

Insert Fig. 3 on Page 325

12.  $K_2TaF_7$  crystals (dry)
13. Na reduction
14. Product
15. Ethanol
16. Na removal
17. Water or hot water
18. Water rinse to remove NaF, KF, NaCl
19. Ta powder
20. Aqua regia
21. Aqua regia rinse
22. HF solution (about 1.5%)
23. HF rinse
24.  $NH_4OH$  solution (about 4%)
25. Ammonia rinse
26. ELS acetone
27. Acetone rinse
28. Drying
29. Ta powder